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Syntheses of Molybdenum and Tungsten Imido Alkylidene Complexes that Contain a Bidentate Oxo/Thiolato Ligand

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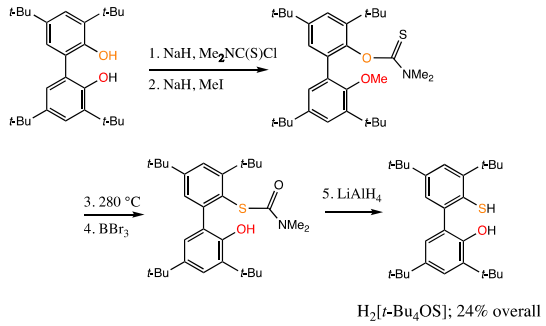
3,3',5,5'-Tetra-*t*-butyl-[1,1'-biphenyl]-2-hydroxy-2'-thiol (H_2[*t*-Bu_4OS]) was prepared in 24% yield overall from the analogous biphenol using standard techniques. Addition of H_2[*t*-Bu_4OS] to Mo(NAr)($CHCMe_2Ph$)(2,5-dimethylpyrrolide)$_2$ led to formation of Mo(NAr)($CHCMe_2Ph$)[*t*-Bu_4OS], which was trapped with PMe_3 to give Mo(NAr)($CHCMe_2Ph$)[*t*-Bu_4OS](PMe_3) (**1**(PMe_3)). An X-ray crystallographic study of **1**(PMe_3) revealed that two structurally distinct square pyramidal molecules are present in which the alkylidene ligand occupies the apical position in each. Both **1**$(PMe_3)_{\mathbf{A}}$ and **1**$(PMe_3)_{\mathbf{B}}$ are disordered. Mo(NAd)($CHCMe_2Ph$)(*t*-Bu_4OS)(PMe_3) (**2**(PMe_3)) and W(NAr)($CHCMe_2Ph$)(*t*-Bu_4OS)(PMe_3) (**3**(PMe_3)) were prepared using analogous approaches. **1**(PMe_3) reacts with ethylene (1 atm) in benzene within 45 minutes to give an ethylene complex (Mo(NAr)(*t*-Bu_4OS)(C_2H_4) (**4**) that is isolable and relatively stable toward loss of ethylene below 60 °C. An X-ray study shows that the bond distances and angles for the ethylene ligand in **4** to be similar to those found for bisalkoxide ethylene complexes of the same general type. Complex **1**(PMe_3) in the presence of one equivalent of $B(C_6F_5)_3$ catalyzes the homocoupling of 1-decene, allyltrimethylsilane, and allylboronic acid pinacol ester at ambient temperature. **1**(PMe_3), **2**(PMe_3), and **3**(PMe_3) all catalyze the ROMP of *rac-endo*,*exo*-5,6-dicarbomethoxynorbornene (*rac*-DCMNBE) in the presence of $B(C_6F_5)_3$, but the polyDCMNBE that is formed has a random structure.

Introduction

Four-coordinate compounds with the formula M(NR)(CHR')(X)(Y) (M = Mo or W), which can be active in a wide variety of selective olefin metathesis reactions, are largely those in which X and Y are monoanionic and oxygen-based (alkoxides, aryloxides, biphenolates, and binaphtholates) or those in which X is oxygen-based and Y is a pyrrolide or a chloride.[1,2] The latter are members of the class of complexes in which the metal is a stereogenic center, a feature that (*inter alia*) has been shown to be required mechanistically for preparing *cis,syndiotactic* polymers from norbornenes.[3] Examples where X and Y are thiolate ligands are relatively rare and they perform poorly in metathesis reactions compared to analogs in which X and Y are oxygen-based.[4] The discovery of metathesis active and *Z*-selective 14e catecholate ruthenium catalysts[5] caused us to explore the synthesis of 14e Mo or W complexes that contain a catecholate (*e.g.*, 3,6-dichlorodithiacatecholate) or other bidentate dithiolate ligand.[6] We prepared several examples of Mo complexes that contain a bidentate dithiolate ligand and found that they too are poor metathesis catalysts. A significant problem continues to be decomposition to give inactive or alkylidene-free complexes through bimolecular decomposition reactions. In this paper we turn to the synthesis of complexes that contain a bidentate "hybrid" alkoxo/thiolate ligand, [*t*-Bu_4OS]$^{2-}$, the dianion formed from 3,3',5,5'-tetra-*t*-butyl-1,1'-biphenyl-2-hydroxy-2'-thiol, H_2[t-Bu_4OS].

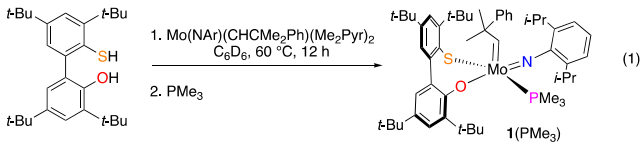
Results and Discussion

The synthesis of H_2[*t*-Bu_4OS] in 24% yield overall that is shown in Scheme 1 follows the relatively standard method for preparing thiophenols from phenols (see Experimental Section).



Scheme 1. Synthetic route to H_2[*t*-Bu_4OS].

Addition of H_2[*t*-Bu_4OS] to Mo(NAr)($CHCMe_2Ph$)(2,5-dimethylpyrrolide)$_2$ leads to formation of Mo(NAr)($CHCMe_2Ph$)[*t*-Bu_4OS], which can be trapped with PMe_3 to give Mo(NAr)($CHCMe_2Ph$)[*t*-Bu_4OS](PMe_3) (**1**(PMe_3)) as orange crystals in 89% yield (eq 1). The ^{1}H NMR spectrum of **1**(PMe_3) in CD_2Cl_2 is characteristic of a C_1 symmetric complex, *i.e.*, four different *t*-Bu resonances are observed for the [*t*-Bu_4OS]$^{2-}$ ligand. The resonance for an *anti* alkylidene α proton is found as a doublet at 14.3 ppm ($^3J_{HP}$ = 5.5 Hz) with a J_{CH} value of 143 Hz. The alkylidene α carbon resonance in **1** (PMe_3) is found as a doublet at 319 ppm ($^2J_{CP}$ = 17.8 Hz). The phosphine ligand is labile enough to be scavenged through addition of $B(C_6F_5)_3$ to **1**(PMe_3) in C_6D_6. One *syn* alkylidene resonance is observed at 10.76 ppm (J_{CH} =121 Hz) in Mo(NAr)($CHCMe_2Ph$)[*t*-Bu_4OS] (**1**).



An X-ray crystallographic study of **1**(PMe_3) reveals that two structurally distinct molecules are present (**1**(PMe_3)$_\mathbf{A}$, Figure 1, and **1**(PMe_3)$_\mathbf{B}$) along with two molecules of diethyl ether. Both **1**(PMe_3)$_\mathbf{A}$ and **1**(PMe_3)$_\mathbf{B}$ are close to being square pyramids (*e.g.*, τ = 0.33 for **1**(PMe_3)$_\mathbf{A}$. The alkylidene ligand occupies the apical position in each and the PMe_3 ligand is bound *trans* to S. Both **1**(PMe_3)$_\mathbf{A}$ and **1**(PMe_3)$_\mathbf{B}$ are disordered. In **1**(PMe_3)$_\mathbf{A}$ (Figure 1) ~24% of the alkylidene is in the *syn* conformation, while in **1**(PMe_3)$_\mathbf{B}$ the disorder is confined to the [*t*-Bu_4OS]$^{2-}$ ligand. It should be noted that only one (*anti*) form of **1**(PMe_3) is observed in solution NMR studies. A full description of the details of this crystallographic study can be found in the Supporting Information.

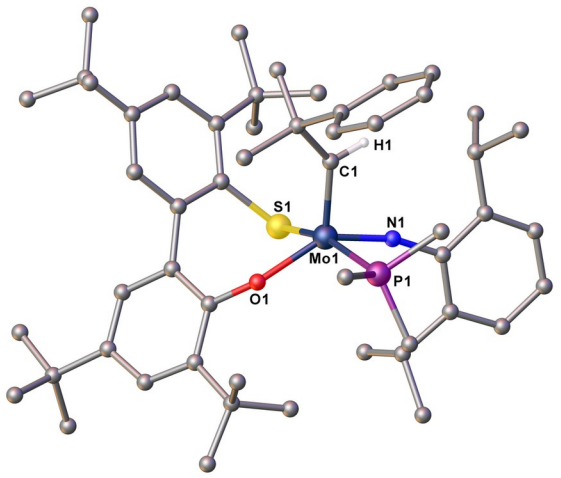


Figure 1. Ball and Stick representation of **1**(PMe_3)$_\mathbf{A}$. All hydrogen atoms (except H1), disordered atoms, and lattice solvent diethyl ether have been omitted for clarity.

The metrical parameters for **1**(PMe_3)$_\mathbf{A}$ and **1**(PMe_3)$_\mathbf{B}$ are comparable to those in analogous molybdenum imido alkylidenes that contain biphenolate or binaphtholate ligands.[1] (See also Table S1 in the SI.) In **1**(PMe_3)$_\mathbf{A}$, Mo=C_α = 1.937(5) Å for the *anti* alkylidene ($\angle$Mo=C_α–C_β = 137.1(4)°) and 1.885(12) Å for the *syn* alkylidene ($\angle$Mo=C_α–C_β = 152.7(13)°). The different Mo-C-C angles for *anti* and *syn* alkylidenes are usually ascribed to an agostic interaction between the C–H bond and the metal in *syn* alkylidenes.[7] The Mo–O bondlength in **1**(PMe_3)$_\mathbf{A}$ is 1.995(3) Å whereas the Mo–S bondlength is 2.4575(9) Å. The $\angle$O–Mo–S bite angle is 86.55(8)° and the dihedral angle between the phenolate and thiophenolate rings in the BiphenSO(*t*-Bu)$_4^{2-}$ ligand is 62.45°.

Heating a mixture of H_2[*t*-Bu_4OS] and Mo(NAd)($CHCMe_2Ph$)(2,5-dimethylpyrrolide)$_2$ (Ad = 1-adamantyl) in benzene at 60 °C for 6 h followed by addition of PMe_3 led to formation of Mo(NAd)($CHCMe_2Ph$)(*t*-Bu_4OS)(PMe_3) (**2**(PMe_3)), which was isolated as a pale yellow solid in 87% yield. Proton NMR studies suggest that **2**(PMe_3) is a mixture of two *syn* alkylidene isomers, which give rise to two doublet alkylidene resonances at -10 °C in toluene-d_8 (Figure 2) at 13.44 ppm (**2**(PMe_3)$_A$, d, J_{HP} = 5.2 Hz, J_{CH} = 119.4 Hz) and 12.77 ppm (**2**(PMe_3)$_B$, d, J_{HP} = 5.4 Hz, J_{CH} = 119.4 Hz) in a ratio of ~1:2. Addition of $B(C_6F_5)_3$ to **2**(PMe_3) produces phosphine-free **2**, which has a singlet *syn* alkylidene resonance in its proton NMR spectrum at 11.76 ppm (J_{CH} = 124.4 Hz) in C_6D_6.

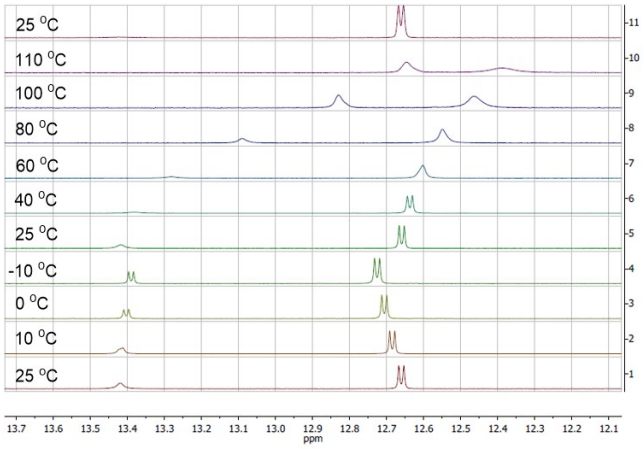


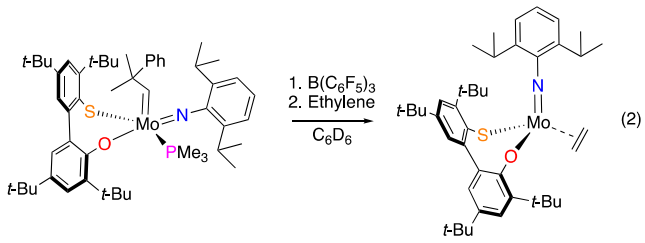
Figure 2. Variable temperature proton NMR spectra of **2**(PMe_3) (400 MHz, toluene-d_8).

Variable temperature proton NMR spectra of **2**(PMe_3) in toluene-d_8 (Figure 2) suggest that PMe_3 is lost first from the complex having the more downfield alkylidene resonance (**2**$(PMe_3)_A$) as a sample is warmed from -10 °C, and the resonance shifts upfield as the percentage of **2** increases. The same behavior is observed for the complex having the more upfield alkylidene resonance (**2**$(PMe_3)_B$), but at higher temperatures. The ratio of the two isomers of **2**(PMe_3) that are in equilibrium with **2** and free PMe_3 is ~1:1 at 110 °C. On the basis of the change in chemical shift of each isomer with T, the amount of **2**$(PMe_3)_A$ in equilibrium with **2** at 110° can be estimated to be ~50%, while the amount of **2**$(PMe_3)_B$ in equilibrium with **2** is ~25%, consistent with a greater lability of PMe_3 in **2**$(PMe_3)_A$. We propose that **2**$(PMe_3)_A$ and **2**$(PMe_3)_B$ are SP isomers in which PMe_3 is *trans* to S or O, respectively. The top spectrum at 25 °C show largely **2**$(PMe_3)_B$ to be present, which suggests that at 25 °C the isomers do not equilibrate readily, but do equilibrate in the process of heating to 110 °C and cooling back to 25 °C, a process that involves dissociation of PMe_3, as just discussed and likely also intramolecular rearrangement of phosphine adducts. The ^1H NMR spectrum of a sample after addition of 1 equiv of $B(C_6F_5)_3$ in 500 µl of C_6D_6 shows that a phosphine-free complex is formed that has a *syn* alkylidene resonance at 11.76 ppm (J_{CH} = 124.4 Hz).

One equivalent of H_2[*t*-Bu_4OS] was added to W(NAr)($CHCMe_2Ph$)(2,5-dimethylpyrrolide)$_2$ in benzene followed by heating the sample at 60 °C. The addition of PMe_3 then led to formation of W(NAr)($CHCMe_2Ph$)(*t*-Bu_4OS)(PMe_3) (3(PMe_3)). The proton NMR spectrum shows 3(PMe_3) to be a mixture of *anti* and *syn* isomers (1:9) with J_{CH} =136 Hz in the *syn* isomer. Orange crystals of 3(PMe_3) were obtained from a solution of 3(PMe_3) in diethyl ether and pentane upon cooling the solution to -20 °C. The reaction between 3(PMe_3) with $B(C_6F_5)_3$ goes to completion over a period of 6h to generate W(NAr)($CHCMe_2Ph$)(*t*-Bu_4OS) (3; $J_{WH\alpha}$ = 13.7 Hz). The relative slow reaction of 3(PMe_3) with $B(C_6F_5)_3$ compared to the reactions between 1(PMe_3) and 2(PMe_3) with $B(C_6F_5)_3$ a more tightly bound PMe_3 in the tungsten complex than in the molybdenum complexes.

Recently, we reported the characterization and some metathesis reactions initiated by Mo(NAr)($CHCMe_2Ph$)(*t*-Bu_4S_2)(PMe_3).[6] We noted that this complex does not tolerate ethylene and therefore decomposes as ethylene builds up during metathesis of terminal olefins. Formation of a Mo ethylene complex was proposed on the basis of NMR studies, but the ethylene complex lost ethylene with time to form uncharacterized decomposition products.

Complex **1** reacts with excess ethylene (1 atm) in benzene within 45 minutes to give an ethylene complex (**4**) that can be isolated as red crystals from a saturated pentane solution at -20 °C (equation 2). Compound **4** is stable in benzene for several days and also after heating its solutions to 60 °C for several hours. However, heating samples above 60 °C results in slow loss of ethylene and decomposition. We did not observe any significant change in the proton NMR spectrum of **4** under 1 atm of ethylene.



(2)

An X-ray study (Figure 3) confirms that **4** is an ethylene complex. Selected bond distances (Å) associated with the ethylene ligand are Mo–C1 = 2.1443(17), Mo–C2 = 2.1976(18), and C1=C2 = 1.420(3). (Complete details can be found in the SI.) Molybdenum(IV) olefin complexes are rare, but several have

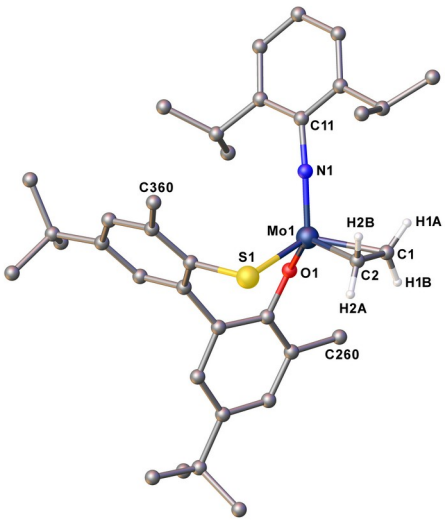


Figure 3. Ball and Stick representation of **4**. All hydrogen atoms, methyl groups on C260 and C360, and disordered atoms have been omitted for clarity (see SI for details).

been prepared and crystallographically characterized.[8] They include Mo(NAr)(C_2H_4)($OSiPh_3$)(Me_2Py), Mo(NAr)(C_2H_4)(Me_2Py)$_2$, and Mo(NAr)(C_2H_4)[$OCH(CF_3)_2$]$_2$(Et_2O). The Mo-$C_{ethylene}$ bond distances and ethylene C-C bond distances in these compounds are similar to those found in **4**. Mo(NAr)((C_2H_4)($OSiPh_3$)$_2$ was found to react reversibly with ethylene to give the molybdacyclopentane complex, Mo(NAr)(C_4H_8)($OSiPh_3$)$_2$. The precise mechanism of reduction of the metal and formation of **4** under ethylene is not known, but most likely consists either of bimolecular decomposition of a methylene complex or rearrangement of an unsubstituted molybdacyclobutane complex to propylene.

Selected metathesis reactions initiated by compounds reported here were surveyed in a preliminary fashion. **1**(PMe_3) in the presence of one equivalent of $B(C_6F_5)_3$ catalyzes the homocoupling of 1-decene, allyltrimethylsilane, and allylboronic acid pinacol ester at ambient temperature. Typical reactions were carried out with 5 mol% catalyst loading except in the reaction that involves 1-decene where the catalyst loading was 1 mol%. The homocoupling reactions proceed to about 90% conversion in 24 h and do not exhibit any special *cis* or *trans* selectivity. Under similar conditions, the homocoupling of 1-decene catalyzed by **2**(PMe_3) proceeds to only about 8% conversion after 20 h.

ROCM reactions between *Z*-cyclooctene and *Z*-dichloroethylene[2a] catalyzed by **1**(PMe_3), **2**(PMe_3), or **3**(PMe_3) in the presence of $B(C_6F_5)_3$ resulted in disappearance of the alkylidene resonance, but no reaction with *Z*-cyclooctene and no cross-metathesis products are observed. However, **1**(PMe_3) and **2**(PMe_3) rapidly catalyze the ring-opening polymerization (ROMP) of *Z*-cyclooctene in the presence of $B(C_6F_5)_3$ at ambient temperature. In the ^{1}H NMR spectrum of polyCOE initiated by **1**(PMe_3), new alkylidene resonances (multiplets) presumably pertaining to Mo=CH(CH_2R) (from the ROMP of COE) are observed at 12.2 and 13.1 ppm. These resonances persist for over 24 h in solution until the addition of *Z*-dichloroethylene, which causes immediate disappearance of the alkylidene resonances. Although no multiplet alkylidene resonances are observed in the ROMP of COE reaction initiated by **2**(PMe_3), similar decomposition occurs when *Z*-dichloroethylene is added.

Complexes **1**(PMe_3), **2**(PMe_3), and **3**(PMe_3) all catalyze the ROMP of *rac-endo,exo*-5,6-dicarbomethoxynorbornene (*rac*-DCMNBE) in the presence of $B(C_6F_5)_3$. In all the cases, the polyDCMNBD that is formed has no single structure. The structure that has been prepared with catalysts that are asymmetric at the metal is *cis,syndiotactic,alt*, in which "alt" refers to the incorporation of enantiomers of DCMNBE in an alternating fashion.[9]

Conclusions

We conclude from this work that molybdenum and tungsten complexes that contain one oxygen and one sulfur in a bidentate biphenolate-like ligand promote olefin metathesis and that an ethylene complex is stabilized against loss of ethylene relative to a complex of this general type that contains two thiolate sulfurs. However, in preliminary studies we find that initiators that contain the *t*-Bu_4OS ligand do not have any obvious advantages over the many initiators that contain two alkoxide oxygens. The catalysts are not especially active or long-lived and the asymmetry at the metal center created by the *t*-Bu_4OS ligand does not allow formation of *cis,syndiotactic*
polyDCMNBE, as found with catalysts that contain the N/O or Cl/O ligand combinations.

Experimental Section

General Procedures

All air- and moisture-sensitive compounds were manipulated under a nitrogen atmosphere in a glovebox or on a Schlenk line. Glassware was oven-dried prior to use. Solvents were degassed and dried by passing through columns of activated alumina or 4Å molecular sieves and stored over activated molecular sieves. Pentane was shaken with sulfuric acid and then rinsed with water in order to remove traces of olefins. Benzene-d_6 and toluene-d_8 were dried over Na/benzophenone, vacuum transferred onto molecular sieves, and stored in the glovebox. Methylene chloride-d_2 was dried over CaH_2, vacuum transferred onto molecular sieves, and

stored in the glovebox. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to the NMR solvent residual peak and ^{31}P $\{^{1}H\}$ spectra were referenced externally to H_3PO_4 in a D_2O standard. $B(C_6F_5)_3$ was purchased from Strem and used as received. PMe_3 was purchased from Strem, degassed, and stored over sieves prior to use. Ultra high purity ethylene was purchased from Airgas and used without further purification. 3,3',5,5'-tetra-*t*-butyl-[1,1'-biphenyl]-2,2'-diol,[10] $Mo(NAr)(CHCMe_2Ph)(Me_2Pyr)_2$,[11] $Mo(NAd)(CHCMe_2Ph)(Me_2Pyr)_2$,[11] and $W(NAr)(CHCMe_2Ph)(Me_2Pyr)_2$[12] were prepared as described in the literature. Elemental Analyses were performed at the Elemental Analysis facility at the University of Rochester, New York, Midwest Microlab, Indiana, and Atlantic Microlab, Georgia.

Synthesis of **3,3',5,5'-tetra-t-butyl-1,1'-biphenyl-2-hydroxy-2'-thiol, H_2[t-Bu_4OS]**

3,3',5,5'-Tetra-*t*-butyl-[1,1'-biphenyl]-2,2'-diol (8.0 g, 1 eq. 19.48 mmol) was dissolved in dry DMF (150 mL) and the mixture was cooled to 0 °C. NaH (514 mg, 1.1 equiv, 21.43 mmol) was added to the solution under a flow of N_2. The cold bath was removed and the mixture was allowed to warm up to room temperature and was stirred for 4 h. Dimethylthiocarbamoyl chloride (9.6 g, 4 equiv. 77.92 mmol) was added in one portion and the mixture was heated at 70 °C for 1.5 days. The mixture was cooled to room temperature and water (200 mL) was and the mixture was shaken vigorously. A white precipitate formed. The mixture was kept at 0 °C for a few hours before filtering off the precipitate. The white precipitate was dissolved in ethyl acetate and the solution was dried over magnesium sulfate. The ethyl acetate solution was filtered and all volatiles were removed *in vacuo* to give 7.52 g (77% yield) of 3,3',5,5'- tetra-*t*-butyl-1,1'-biphenyl-2-hydroxy-2'-oxy-dimethylthiocarbamoyl.

Crude 3,3',5,5'- tetra-*t*-butyl-1,1'-biphenyl-2-hydroxy-2'-oxy-dimethylthiocarbamoyl (5.5 g) was dissolved in dry DMF and sodium hydride (371 mg, 1.4 equiv, 15.47 mmol) was added under a flow of N_2 while the DMF solution was kept at 0 °C. After bubbling had stopped completely, methyl iodide (0.9 mL, 1.4 eq., 15.47 mmol) was added via syringe. The mixture was heated to 40 °C and stirred for 6 h. The mixture was cooled to room temperature and water (200 mL) was added. The white precipitate was filtered off and purified through column chromatography (DCM/hexane 90/10) to give 4.96 g of 3,3',5,5'- tetra-*t*-butyl-1,1'-biphenyl-2-methoxy-2'-oxy-dimethylthiocarbamoyl (56%). Alternatively, the product can be extracted from the crude mixture with cold methanol: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 (d, $^{4}J_{HH}$=2.7, 1H), 7.28 (d, $^{4}J_{HH}$=2.7, 1H), 7.25 (d, $^{4}J_{HH}$=2.7, 1H), 7.20 (d, $^{4}J_{HH}$ = 2.7, 1H), 3.15 (s, 3H), 3.10 (s, 3H), 3.05 (s, 3H), 1.43 (s, 9H), 1.39 (s, 9H), 1.35 (s, 9H), 1.32 (s, 9H); $^{13}C\{^{1}H\}$ ($CDCl_3$, 100.6 MHz): 186.5, 154.5, 148.1, 147.9, 144.0, 140.6, 140.0, 134.7, 131.3, 129.7, 127.2, 123.4, 122.9, 60.0, 42.7, 38.6, 35.3, 35.2, 34.7, 34.5, 31.6, 31.5, 31.3, 31.1. HRMS (m/z) Calcd for $C_{32}H_{50}NO_2S$ [M+H]: 512.3562, found: 512.3570.

A solid 4 g sample of 3,3',5,5'- tetra-*t*-butyl-1,1'-biphenyl-2-methoxy-2'-oxy-dimethylthiocarbamoyl (7.81 mmol) was heated to 280 °C under N_2 (ballon) for 45 minutes. The mixture was cooled to room temperature, the brown solid was dissolved in dichloromethane (100 mL), and the solution was passed through a frit into a dry Schlenk flask. The solution was cooled to 0 °C and (under N_2) a 1 M solution of BBr_3 in dichloromethane (16 mL, 2 equiv, 15.63 mmol) was added dropwise via syringe at 0 °C. The ice bath was removed and the solution was stirred for one day, after which 5% HCl in water (100 mL) was added slowly. The organic phase was separated and the aqueous phase was washed with dichloromethane (2x, 100 mL each). The combined organic portion was washed with brine and dried over magnesium sulfate. The mixture was filtered and all volatile components were removed *in vacuo*. The crude product was dissolved in minimum ethanol and kept at 0 °C to yield the product as a white microcrystalline precipitate of 3,3',5,5'-tetra-*t*-butyl-1,1'-biphenyl-2-hydroxy-2'-thio-dimethylcarbamoyl; yield 2.90 g, (75%): ^{1}H NMR ($CDCl_3$, 400 MHz): 7.6 (d, $^{4}J_{HH}$=2.2, 1H), 7.3 (broad s, 1H), 7.2 (broad s, 1H), 6.9 (broad s, 1H), 2.8 (broad s, 6H), 1.5 (s, 9H), 1.4 (s, 9H), 1.34 (s, 9H), 1.30 (s, 9H); $^{13}C\{^{1}H\}$ ($CDCl_3$, 100.6 MHz): 154, 152, 150, 147, 141, 137, 131, 128, 127, 125, 124, 122, 37.4, 37.0 (broad), 35, 34, 32, 31.52, 31.46, 30. HRMS (m/z) Calcd for $C_{31}H_{48}NO_2S$ [M+H]: 498.3406, found: 498.3409.

$LiAlH_4$ (1.3 g, 6 eq., 34.95 mmol) was added to a solution of the above compound (2.9 g, 1 equiv., 5.82 mmol) in dry THF (100 mL) under a flow of N_2. The mixture was heated to reflux for 4 hours. The solution was cooled to room temperature and then to 0 °C and degassed water was added. The organics were extracted into diethyl ether (3x, 50 mL each). The diethyl ether extract was dried over magnesium sulfate and the solution was filtered. All volatiles were removed under reduced pressure. The yellow residue was dissolved in minimum hot ethanol and left standing at room temperature overnight. The white precipitate of 3,3',5,5'-tetra-*t*-butyl-1,1'-biphenyl-2-hydroxy-2'-thiol (H_2[t-Bu_4OS]) was isolated by filtration; yield 1.41 g, 57%: ^{1}H NMR ($CDCl_3$, 400 MHz): 7.5 (d, $^{4}J_{HH}$ =2.3 Hz, 1H), 7.4 (d, $^{4}J_{HH}$ =2.5 Hz, 1H), 7.2 (d, $^{4}J_{HH}$ =2.3 Hz, 1H), 7.0 (d, $^{4}J_{HH}$ =2.5 Hz, 1H), 5.0 (s, 1H), 3.8 (s, 1H), 1.6 (s, 9H), 1.5 (s, 9H), 1.33 (s, 9H), 1.32 (s, 9H); $^{13}C\{^{1}H\}$ ($CDCl_3$, 100.6 MHz): 149, 148, 147, 143, 136.4, 136.0, 129.0, 128.7, 126, 125.1, 124.7, 124.2, 37, 35.3, 34.9, 34.6, 32, 31, 30.0, 29.8. HRMS (m/z)

calcd for $C_{28}H_{42}OS$ $[M]^+$: 426.2956, found: 426.2957.

Synthesis of **Mo(NAr)(CHCMe$_2$Ph)(*t*-Bu$_4$OS)(PMe$_3$) (1(PMe$_3$))**

Mo(NAr)(CHCMe$_2$Ph)(2,5-dimethylpyrrolide)$_2$ (300 mg, 0.51 mmol, 1 equiv) and H_2[*t*-Bu$_4$OS] (216 mg, 0.51 mmol, 1 equiv) were dissolved in 20 mL of benzene. The vessel was sealed and heated at 60 °C for 12 h. The volatiles were removed *in vacuo* with gentle heating (~ 40 °C). The solid was triturated with 10 mL of pentane and filtered and dried *in vacuo*. Inside the glovebox, PMe_3 (77 mg, 1.01 mmol, 2 equiv) in 20 mL of pentane was added to the dry residue and the solution was stirred for 10 minutes. The volatiles were removed from the dark orange solution and the resulting solid was dissolved in minimum pentane. The solution was stored at -20 °C overnight to give orange crystals of **1**(PMe_3); yield 383 mg in two crops (89%): ^{1}H NMR (CD_2Cl_2, 400 MHz): (anti alkylidene):14.3 (d, $^1J_{CH}$ =143.0 Hz, $^3J_{HP}$ =5.5 Hz, 1H), 7.39 (d, $^4J_{HH}$ =2.3 Hz, 1H), 7.37-7.33 (m, 3H), 7.30-7.25 (m, 3H), 7.20-7.13 (m, 4H), 6.87 (d, $^4J_{HH}$ =2.7 Hz, 1H), 4.21 (broad s, 1H), 3.57 (broad s, 1H), 1.61 (s, 9H), 1.57 (s, 3H), 1.54 (s, 9H), 1.46 (broad s, 3H), 1.36 (s, 9H), 1.35 (s, 9H), 1.26 (broad s, 9H), 0.95 (d, $^2J_{HP}$ =8.2 Hz, 9H), 0.59 (s, 3H); ^{13}C{^{1}H} (CD_2Cl_2, 100.6 MHz): 319 (d, $^2J_{HP}$ =17.8 Hz), 161, 152 (d, J_{HP} =2.3 Hz), 149.6 (broad), 149.2 (d, J_{HP} =2.7 Hz), 147.8, 147.4 (broad), 147.1, 146, 141, 140 (d, d, J_{HP} =2.2 Hz), 138 (d, d, J_{HP} =2.3 Hz), 137, 130, 128.3, 127.8, 127, 126.2, 125.8, 123.4, 123.2, 122, 53, 38, 35, 34.3, 34.1, 31.4, 31.3, 30.8, 30.5, 30.1, (broad), 29 (broad), 27, 26 (broad), 25 (broad), 23 (broad), 22 (broad), 17 (d, $^2J_{H\text{-}P}$=21.3 Hz), 14; ^{31}P{^{1}H} NMR (CD_2Cl_2, 162.0 MHz): -16.2. Anal. Calcd for $C_{53}H_{78}MoNOPS$: C, 70.40%; H, 8.70%; N, 1.55%. Found: C, 70.48%; H, 8.72%; N, 1.60%.

$B(C_6F_5)_3$ (6 mg, 0.01 mmol, 1 equiv) and **1**(PMe_3) (10 mg, 0.01 mmol, 1 equiv) were dissolved in 0.5 mL C_6D_6 in order to generate **1**, whose ^{1}H NMR spectrum shows one *syn* alkylidene resonance at 10.76 ppm (J_{CH} =121.4 Hz).

Synthesis of **Mo(NAd)(CHCMe$_2$Ph)(*t*-Bu$_4$OS)(PMe$_3$) (2(PMe$_3$))**

Mo(NAd)(CHCMe$_2$Ph)(2,5-dimethylpyrrolide)$_2$ (200 mg, 0.35 mmol, 1 equiv) and H_2[*t*-Bu$_4$OS] (151 mg, 0.35 mmol, 1 equiv) were dissolved in 10 mL of benzene and the vessel was sealed and heated at 60 °C for 6 h. The volatiles were removed *in vacuo* with gentle heating (~ 40 °C). Inside the glovebox, PMe_3 (54 mg, 0.70 mmol, 2 equiv) in 10 mL of pentane was added to the dry residue and the dark yellow solution was stirred for 15 minutes. All volatiles were removed *in vacuo* with gentle heating. The resulting dark yellow solid was washed with cold pentane (4 mL) to yield **2**(PMe_3); yield 269 mg (87%): ^{1}H NMR (CD_2Cl_2, 400 MHz) (*syn* alkylidene) δ 12.39 (d, $^1J_{CH}$ =120.7 Hz, $^3J_{HP}$ =5.0 Hz, 1H), 7.32-7.28 (m, 2H), 7.26 (d, $^4J_{HH}$ =2.7 Hz, 1H), 7.20-7.14 (m, 2H), 7.11-7.06 (m, 3H), 6.66 (d, $^4J_{HH}$ =2.7, 1H), 2.13-1.97 (m, 12H), 1.67 (s, 6H), 1.64 (s, 9H), 1.46 (s, 9H), 1.37 (s, 9H), 1.31 (s, 9H), 0.99 (d, $^2J_{HP}$ =9.1 Hz, 9H), 0.75 (s, 3H); ^{13}C{^{1}H} (CD_2Cl_2, 100.6 MHz): 303.3, 162.8, 148.8 (d, J_{CP} =3.7 Hz), 146.6, 145.0, 144.6, 144.5, 138.8, 137.0, 135.7, 128.3, 128.1, 126.0, 125.4, 125.2, 123.2, 121.5, 72.3, 49.6, 44.5, (d, J_{CP} =2.2 Hz), 37.3, 35.9, 35.2, 34.4, 34.0, 32.7, 32.6, 31.5, 31.1, 30.5, 29.6, 28.1, 16.6 (d, $J_{C\text{-}P}$=22.2 Hz); ^{31}P{^{1}H} NMR (CD_2Cl_2, 162.0 MHz): -11.2. Anal. Calcd for $C_{51}H_{76}MoNOPS$: C, 69.76%; H, 8.72%; N, 1.60%. Found: C, 70.19%; H, 9.28%; N, 1.58%.

The temperature dependent proton NMR spectra of **2**(PMe_3) are shown in Figure 2 and described in the text.

Synthesis of **W(NAr)(CHCMe$_2$Ph)(*t*-Bu$_4$OS)(PMe$_3$) (3(PMe$_3$))**

W(NAr)(CHCMe$_2$Ph)(2,5-dimethylpyrrolide)$_2$ (200 mg, 0.29 mmol, 1 equiv) and H_2[*t*-Bu$_4$OS] (126 mg, 0.29 mmol, 1 equiv) were dissolved in 10 mL of benzene. The solution was transferred to a Schlenk flask and a stir bar was added. The flask was sealed and heated at 60 °C for 24h. The volatiles were removed *in vacuo* and the residue was triturated with pentane and all volatiles again removed *in vacuo*.. The yellow powder was redisssolved in 10 mL of pentane, a solution of PMe_3 in 5 mL of pentane was added, and the mixture was stirred for 15 minutes. After removal of volatiles *in vacuo*, the solid was dissolved in minimum Et_2O and the same volume of pentane was added. The mixture was kept at -20 overnight and orange crystals were filtered off; yield 160 mg (55%): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 12.55 (d, $^2J_{HP}$ = 4.7 Hz, $^1J_{CH}$ = 136 Hz, 1H, W=CH_{anti}), 11.32 (d, $^2J_{HP}$ = 3.2 Hz, $^1J_{CH}$ = 115 Hz, $^2J_{HW}$ = 14 Hz, W=CH_{syn}), 7.43 (d, $^3J_{HH}$ = 2.3 Hz, 1H), 7.44 (d, $^3J_{HH}$ = 2.8 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.32 (s, 1H), 7.33 – 7.27 (m, 2H), 7.24 – 7.06 (m, 4H), 6.94 (d, $^3J_{HH}$ = 2.7 Hz, 1H), 4.18 (s, 1H, *i*-Pr methine), 3.52 (s, 1H, *i*-Pr methine), 1.65 (s, 9H, *t*-Bu), 1.58 (s, 9H, *t*-Bu), 1.39 (overlapping s,18H, *t*-Bu), 1.45 (s, 3H, *Me*), 1.12 (d, *J* = 8.7 Hz, 9H, P*Me*$_3$), 0.63 (s, 3H, *Me*) ppm. (The methyl resonances from the NAr ligand are broadand overlap with one another); ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) δ 295.3 (d, $^2J_{CP}$ = 11.8 Hz, W=*C*), 160.7, 152.0, 151.8 (d, J_{CP} = 2.8 Hz), 148.0, 147.7, 146.6, 141.9, 139. 9, 137.7, 137.5, 130.3, 128.7, 127.7, 126.9, 126.4, 123.9, 122.6, 118.6, 106.1, 51.4 (d, J = 2.5 Hz), 37.9, 35.7, 34.7, 34.5, 34.2 (d, J_{CP} = 4.0 Hz), 31.8, 31.7, 31.3, 31.0, 30.0, 29.9 (broad), 29.8, 28.2, 28.0 (broad), 26.6 (broad), 25.0 (broad), 23.5 (broad), 22.9 (broad), 22.6, 17.9 (d, $^1J_{CP}$ = 26.0 Hz) ppm; ^{31}P{^{1}H} NMR (203 MHz, CD_2Cl_2) δ –5.71 ($^1J_{PW}$ = 285.1 Hz) ppm. Anal.

Calcd for $C_{53}H_{78}NOPSW$: C, 64.17%; H, 7.93%; N, 1.41%. Found: C, 63.97%; H, 8.07%; N, 1.54%.

Synthesis of **Mo(NAr)(CH_2CH_2)(*t*-Bu_4OS) (4**)

1(PMe_3) (80 mg, 0.09 mmol, 1 equiv) and $B(C_6F_5)_3$ (45 mg, 0.09 mmol, 1 equiv) were placed in a vial and benzene (2 mL) and pentane (5 mL) were added. The mixture was stirred for 45 minutes and filtered through a fine porosity frit into a Schlenk flask. On a Schlenk line, the solution was degassed and exposed to 1 atm of ethylene. After 45 minutes of exposure to ethylene, all volatiles were removed from the solution and 5 mL of pentane were added to the residue and the solution was kept at -20 °C. Red microcrystals of the product formed right above the solution over a period of several days through capillary crystallization. The solution was carefully removed and the ethylene complex isolated as a red microcrystalline powder; yield 30 mg (47%): ^{1}H NMR (C_6D_6, 400 MHz): 7.6 (d, $^4J_{HH}$ =2.3 Hz), 7.5 (d, $^4J_{HH}$ =2.3 Hz), 7.32 (d, $^4J_{HH}$ =2.3 Hz), 7.29 (d, $^4J_{HH}$ =2.3 Hz), 6.94-6.88 (m, 3H), 3.6 (m, 1H), 3.2 (septet, $^3J_{HH}$ =6.9 Hz), 3.0 (m, 1H), 2.7 (m, 1H), 2.0 (m, 1H), 1.5 (s, 9H), 1.4 (s, 9H), 1.3 (s, 9H), 1.21 (s, 9H), 1.20 (d, $^3J_{HH}$ =6.9 Hz), 0.9 (d, $^3J_{HH}$ =6.9 Hz); ^{13}C{^{1}H} (CD_2Cl_2, 100.6 MHz) observed in gHMBC and gHSQC spectra: 160.0, 154.9, 151.8, 150.4, 147.9, 144.4, 142.5, 139.7, 135.4, 132.4, 128.7, 127.4, 126.4, 124.2, 122.6, 122.5, 56.7, 55.5, 38.3, 32.2, 30.9, 30.6, 30.4, 29.8, 22.5.

Upon heating a 10 mg sample of ethylene complex in 500 μL of toluene-d_8 (0.02 M), no change in the ^{1}H NMR spectrum was observed up to 70 °C. However, above 60 °C, free ethylene was observed and the compound began to decompose in an unidentified manner.

Procedure for Homocoupling Reactions

In the glovebox, a 1-dram vial was charged with a stir bar, 0.01 mmol of the solid catalyst (5 mol %, ~ 5 mg), 10 μL of 1,3,5-trimethoxybenzene (0.5 M in C_6D_6), and diluted with 200 μL of toluene-d_8. One equivalent of $B(C_6F_5)_3$ (0.01 mmol; ~ 3 mg) dissolved 100 μL of toluene-d_8 was added to the catalyst solution and the solution was rapidly stirred. After approximately 30 sec of stirring, 0.20 mmol of the terminal olefin substrate was added and the vial was loosely capped to allow for the generated ethylene to escape. 30 μL aliquots were withdrawn periodically and diluted with 0.7 mL of wet $CDCl_3$ to monitor reaction progress. Conversion and selectivity (%E vs %Z) were determined using ^{1}H NMR spectroscopy.

Procedure for Ring Opening Metathesis Polymerization of Z-Cyclooctene

In the glovebox, a 1-dram vial was charged with **1**(PMe_3) (3 mg, 3.3 μmol, 1 equiv) and the mixture was diluted with 0.4 mL of C_6D_6. To this solution, $B(C_6F_5)_3$ (2 mg, 3.9 μmol, 1.2 equiv) dissolved in 0.3 mL of C_6D_6 was. After approximately 30 seconds *Z*-Cyclooctene (9 μL, 7.6 mg, 20.8 equiv) was added and the solution was mixed thoroughly before transferring to a sealable J-Young NMR tube. ^{1}H NMR spectra were acquired at various time points to monitor reaction progress. The same procedure was followed when the anamantyl analog was used as the initiator.

Procedure for the Ring-opening metathesis polymerization of rac-endo,exo-5,6-dicarbomethoxynorbornene (rac-DCMNBE)

In the glovebox, a 20 mL scintillation vial was charged with **1**(PMe_3) (5 mg, 5.5 μmol, 1 equiv) and solution was diluted with 0.5 mL of toluene. A stir bar and $B(C_6F_5)_3$ (3 mg, 5.9 μmol, 1.1 equiv) dissolved in 0.5 mL of toluene were added. *rac*-DCMNBE (60 mg, 285.4 μmol, 51.6 equiv) dissolved in 0.5 mL of toluene was added to the rapidly stirred solution. After 2 h, the vial was brought out of the glovebox, exposed to air, and added dropwise to 100 mL of stirring methanol. The precipitated polymer was collected on a medium porosity frit, washed with methanol, and dried on a high vacuum Schlenk line; yield 54 mg (84%). ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were acquired in $CDCl_3$.

The same procedure was adopted using either the W(NAr) or Mo(NAd) analogs.

Supplementary Material

Supporting Information NMR spectra for all compounds and details of the X-ray studies for three complexes.

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HT performed most synthetic reactions while CT and PM performed all X-ray structural studies.

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Notes

The authors declare no competing financial interest.

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References

[1] (a) R. R. Schrock, 'High Oxidation State Multiple Metal-Carbon Bonds', *Chem. Rev.* **2002**, *102*, 145-180. (b) R. R. Schrock, A. H. Hoveyda, 'Discovery and Development of Molybdenum and Tungsten Imido Alkylidene Complexes as Efficient Olefin Metathesis Catalysts for use in Organic Synthesis', *Angew. Chem. Int. Ed.* **2003**, *42*, 4592-4633. (c) R. R. Schrock, 'Recent Advances in High Oxidation State Mo and W Imido Alkylidene Chemistry', *Chem. Rev.* **2009**, *109*, 3211–3226. (d) R. R. Schrock, 'High Oxidation State Molybdenum and Tungsten Complexes Relevant to Olefin Metathesis', *Handbook of Metathesis*, Vol 1, 2nd Ed., Wiley-VCH, Weinheim, R. H. Grubbs and A. G. Wenzel, Ed., 2015, pp. 1-32.

[2] (a) J. K. Lam, C. Zhu, K. V. Bukhryakov, R. R. Schrock, P. Müller, A. H. Hoveyda, 'Synthesis and Evaluation of Molybdenum and Tungsten Monoaryloxide Halide Alkylidene Complexes for *Z*-Selective Cross Metathesis of Cyclooctene and *Z*-1,2-Dichloroethylene'. *J. Am. Chem. Soc.* **2016**, *138*, 15774-15783. (b) K. V. Bukhryakov, S. VenkatRamani, C. Tsay, A. H. Hoveyda, R. R. Schrock, 'Syntheses of Molybdenum Adamantylimido and *t*-Butylimido Alkylidene Chloride Complexes Using HCl and Diphenylmethylphosphine', *Organometallics* **2017**, *36*, 4208-4214. (c) M. J. Koh, T. T. Nguyen, J. Lam, S. Torker, J. Hyvl, R. R. Schrock, A. H. Hoveyda, 'Molybdenum Chloride Complexes as Catalysts for Stereoselective Olefin Metathesis', *Nature* **2017**, *542*, 80-85.

[3] (a) E. S. Jang, J. M. John, R. R. Schrock, 'Synthesis of *Cis,syndiotactic*-A-*alt*-B Copolymers from Two Enantiomerically Pure *trans*-2,3-Disubstituted-5,6-Norbornenes', *ACS Cent. Sci.* **2016**, *2,* 631-636. (b) E. S. Jang, J. M. John, R. R. Schrock, 'Synthesis of *Cis,syndiotactic*-**A**-*alt*-**B** Copolymers from Enantiomerically Pure *Endo*-2-Substituted-5,6-Norbornenes', *J. Am. Chem. Soc.* **2017**, *139*, 5043–5046.

[4] (a) J. S. Murdzek, L. Blum, R. R. Schrock, 'Tungsten and Molybdenum Alkylidyne Complexes Containing Bulky Thiolate Ligands', *Organometallics* **1988**, *7*, 436-441. (b) E. M. Townsend, J. Hyvl, W. P. Forrest, R. R. Schrock, P. Müller, A. H. Hoveyda, 'The Synthesis of Molybdenum and Tungsten Alkylidene Complexes that Contain Sterically Demanding Aryl Thiolate Ligands', Organometallics **2014**, *33*, 5334-5341. (c) V. Mougel, M. Pucino, C. Copéret, 'Strongly σ Donating Thiophenoxide in Silica-Supported Tungsten Oxo Catalysts for Improved 1-Alkene Metathesis Efficiency', *Organometallics* **2015**, *34*, 551-554.

[5] (a) M. J. Koh, R. K. M. Khan, S. Torker, A. H. Hoveyda, 'Broadly Applicable Z- and Diastereoselective Ring-Opening/Cross-Metathesis Catalyzed by a Dithiolate Ru Complex', *Angew. Chem. Int. Ed.* **2014**, *53*, 1968-1972. (b) R. K. M. Khan, S. Torker, A. H. Hoveyda, 'Readily Accessible and Easily Modifiable Ru-Based Catalysts for Efficient and Z-Selective Ring-Opening Metathesis Polymerization and Ring-Opening/Cross-Metathesis', *J. Am. Chem. Soc.* **2013**, *135*, 10258-10261. (c) C. Xu, Z. Liu, S. Torker, X. Shen, D. Xu, A. H. Hoveyda, 'Synthesis of *Z*- or *E*-Trisubstituted Allylic Alcohols and Ethers by Kinetically Controlled Cross-Metathesis with a Ru Catechothiolate Complex', *J. Am. Chem. Soc.* **2017**, *139*, 15640-15643.

[6] H. Tafazolian, C. Tsay, R. R. Schrock, P. Müller, 'Synthesis of Molybdenum(VI) Imido Alkylidene Complexes that Contain a Bidentate Dithiolate Ligand', *Organometallics* **2018**, *37*, 4024-4030

[7] S. S. Zhu, D. R. Cefalo, D. S. La, J. Y. Jamieson, W. M. Davis, A. H. Hoveyda, R. R. Schrock, 'Chiral Mo-Binol Complexes: Synthesis, Structure, Activity. Efficient Enantioselective Six-Membered Ring-Synthesis Through Catalytic Metathesis', *J. Am. Chem. Soc.* **1999**, *121*, 8251−8259.

[8] S. C. Marinescu, A. J. King, R. R. Schrock, R. Singh, P. Müller, M. K. Takase, 'Simple Molybdenum(IV) Olefin Complexes of the Type Mo(NR)(X)(Y)(olefin)', *Organometallics* **2010**, *29*, 6816-6828.

[9] (a) D. H. McConville, J. R. Wolf, R. R. Schrock, 'Synthesis of Chiral Molybdenum ROMP Initiators and All-Cis Highly Tactic Poly-2,3-R_2 Norbornadiene (R = CF_3 or CO_2Me)', *J. Am. Chem. Soc.* **1993**, *115*, 4413-4414. (b) R. R. Schrock, 'Synthesis of stereoregular ROMP polymers using molybdenum and tungsten imido alkylidene initiators', *Dalton Trans.* **2011**, *40*, 7484-7495. (c) R. R. Schrock, 'Synthesis of Stereoregular Polymers through Ring-Opening Metathesis Polymerization', *Acc. Chem. Res.* **2014**, *47*, 2457-2466.

[10] T. Yamato, K-I. Hasegawa, Y. Saruwatari, L. K. Doamekpor, 'Novel Spherand-Type Calixarenes – Synthesis, Conformational Studies, and Isomer Separation', *Chem. Ber*. **1993**, *126*, 1435-1439.

[11] R. Singh, C. Czekelius, R. R. Schrock, P. Müller, 'Molybdenum Imido Alkylidene Metathesis Catalysts that Contain Electron Withdrawing Biphenoxides or Biphenolates', *Organometallics* **2007**, *26*, 2528-2539.

[12] T. Kreickmann, S. Arndt, R. R. Schrock, P. Müller, 'Imido Alkylidene Bispyrrolyl Complexes of Tungsten', *Organometallics* **2007**, *26*, 5702-5711.